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Comparison of Adsorption and Selectivity Characteristics for 4-Nitrophenol Imprinted Polymers Prepared via Bulk and Suspension Polymerization

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ABSTRACT

This manuscript describes a method for the selective removal of phenolic compounds from aqueous medium by imprinted polymers, which is the noncovalent approach based on both hydrogen bonding and hydrophobic interaction. These imprinted polymers were prepared by both bulk polymerization (IP1) and suspension polymerization (IP2) of methacryloylantipyrine (MAAP) in the presence of azobisisobutyronitrile (AIBN) as an initiator and cross-linking EGDMA and was imprinted with

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4-nitrophenol. The effect of polymerization technique (bulk and suspension) on the adsorption and selectivity of phenolics was investigated. The maximum adsorption capacities of these IP1 and IP2 polymers were 25.9 and 27.6 mg/g for 4-nitrophenol, respectively. It was observed that the 4-nitrophenol binding capacity decreased with increasing pH. The selectivity experiments showed that the polymer prepared via suspension polymerization has high-binding ability for 4-nitrophenol to other phenolics compared to the polymer prepared via bulk polymerization.

Key Words: Phenol; Adsorption of phenol; Molecularly imprinted polymer (MIP); Bulk and suspension polymerization.

INTRODUCTION

Phenolic compounds have interested different researchers because of their physiological and physical-chemical properties as well as their anticarcinogenic and high-antioxidant capacity. These compounds are polluting substances present in the aquatic environment as by-products of the coal and oil industry or the result of pesticide and drug decay.[1] The U.S. Environmental Protection Agency (EPA) and European Union have included phenol and various chlorophenols and nitrophenols in their lists of priority pollutants to be monitored in the aquatic environment. The maximum level allowed for these compounds in publicly supplied water is 0.5 μg/mL. Because of their carcinogenic properties there is a great need in wastewater for a new and selective technique for phenol separation.

The removal and/or detoxification of phenolic compounds can be done by microbial degradation, and chemical oxidation using agents such as ozone, hydrogen peroxide, or chlorine dioxide. The main limitation of these methods is their low efficiency in the removal of trace levels of phenols. Adsorption is a well-known removal technique for organic compounds from water. The use of activated carbon as an adsorbent for the removal of phenolic compounds is common practice.[2–4] The adsorption behavior of various phenols by polymeric adsorbents and ion exchange resin,[5–7] use of clay and organoclay as an adsorbent,[8,9] and molecularly imprinted adsorbents[10,11] have been studied for the adsorption of phenol from aqueous solution.

Molecular imprinting is a method for making selective binding sites in synthetic polymers by using molecular template. Target molecules (i.e., phenolics) can be used as templates for imprinting cross-linked polymers. After the removal of the template, the remaining polymer is more selective. The selectivity of the polymer depends on various factors such as the size

and shape of the cavity and rebinding interactions. Covalent interactions,[10,12] noncovalent interactions such as hydrogen bonding,[11,13,14] π-π bonding and hydrophobic interaction,[15] electrostatic interactions,[16] and metal ion coordination[17–19] can be exploited to organize the functional monomers around the template. MIPs prepared by suspension and bulk polymerization have been synthesized. Imprinted polymers are usually prepared by bulk polymerization using thermal or UV radiation, but polymerized particles limited mass transfer. MIPs prepared by suspension polymerization are more suitable products for separation strategies.

The objective of this study is to investigate the adsorption behavior of 4-nitrophenol and phenolic compounds on imprinted polymers prepared by both bulk polymerization (IP1) and suspension polymerization (IP2). For this purpose, methacryloylantipyrine (MAAP) monomer, which has π electron-rich aromatic ring, firstly was synthesized by our group using antipyrine, which is hydroxy radical capture and spectroscopic reagent for phenols, and then was polymerized. The 4-nitrophenol, which has an electron-poor aromatic ring, was chosen as a template molecule. Phenol, chlorophenol, 2-nitrophenol, and cresol were used as adsorbates because they are some of the organic pollutants that need to be removed from wastewater. Association constant (K_{ass}), number of accessible sites (N), and binding ability were also evaluated to get information about the specific interaction between 4-nitrophenol imprinted polymers (IP1 and IP2) and 4-nitrophenol.

EXPERIMENTAL

Materials

Both 4-aminoantipyrine and pyridine were supplied by Aldrich and used as received. Ethyleneglycoldimethacrylate (EGDMA) was obtained from Fluka A.G., distilled under reduced pressure in the presence of hydroquinone inhibitor, and stored at 4°C until use. Azobisisobutyronitrile (AIBN), phenol, and p-nitrophenol were also obtained from Fluka. The 4-nitrophenol, 2-chlorophenol were supplied from Aldrich, o-cresol, sodium dihydrogen phosphate were supplied from Riedel-de Haen, and sodium tetraborate was supplied from Codex. Methacryloylchloride was obtained from Sigma. All other chemicals were of reagent grade and were purchased from Merck AG. All water used in the experiments was purified using a Barnstead (Dubuque, IA) ROpure LP reverse osmosis unit with a high-flow cellulose acetate membrane (Barnstead D2731) followed by a Barnstead D3804 NANO pure organic/colloid removal and ion exchange packed-bed system.

Instrumentation

Capillary electrochromatography experiments were carried out with a Prince CEC 760 model 3D capillary electrochromatography system, equipped with a diode-array detector. Uncoated fused-silica capillary (75 μm ID) with a total length of 35.0 cm was used for the MECC separations. The capillary was conditioned before use and between runs with 0.2 M NaOH and rinse buffer for 20 min. Inlet buffer injection was performed for 0.2 sec at 100 mbar, analyte for 0.1 sec at 20 mbar, the detection wavelength was 210 nm, and the separation voltage was maintained at 15 kV. The concentration of phenolic compounds was 50 ppm. Phosphate-borate buffer with pH 7.0 was selected for optimization experiments and sodium dodecyl sulfate was used as a surfactant. The column temperature was maintained at 25°C. Automated capillary rinsing, sample introduction, and execution of the electrophoretic runs were controlled by a personal computer. Data processing was carried out with a Dax.7.1 3D software. Three replicate runs were performed for all conditions.

Fourier transform infrared spectroscopy (FTIR) spectra of P(MAAP-co-EGDMA) and microbeads were obtained through the use of a FTIR spectrophotometer (Jasco Corparation, made in Japan; FT/IR-300 E). A Fisher Scientific, Accumet® Basic AB15 pH-meter was used to measure pH values.

Synthesis of MAAP

The following experimental precedure was applied for the synthesis of MAAP:[20] 4-aminoantipyrine (0.5 g; 2.463 mmol) and pyridine (0.2 mL; 2.46 mmol) were dissolved in 100 mL of dry $CHCl_3$ and the solution was cooled to 0°C. Then, methacryloylchloride (0.26 mL; 2.46 mmol) was poured slowly into this solution by stirring magnetically at room temperature for 2 h. At the end of this chemical reaction period, the solution was washed with dilute 50 mL of HCl and 50 mL of dilute NaOH. Then, the organic phase was evaporated in a rotary evaporator. The residue was crystallized in petroleumbenzene-ethylacetate.

Melting point was found at 132–133°C, Yield % 70. FT-IR (KBr, cm^{-1}): 770–710 cm^{-1} (monosubstituted benzene ring), 1580–1500 cm^{-1} (conjugation at aromatic ring, strong two or three bands), 1600 cm^{-1} (methacryl double-band), 1642 cm^{-1} (amide carbonyl band), 1730 cm^{-1} (carbonyl band at cyclis ketone position), 2975–2925 cm^{-1} (C—H band), 3260 cm^{-1} (N═H band). 1H-NMR ($CHCl_3$): 2.05 ppm 3H singlet (—C═C—CH_3, vinyl methyl), 3.0 ppm 3H singlet (—C—CH_3), 3.35 ppm 3H singlet (—N—CH_3), 5.5 ppm 1H singlet (—CH_a═C—), 5.8 ppm 1H singlet (—CH_b═C—), 7.25–8.80 ppm 4H multiplet (aromatic, $CDCl_3$ peak is also

observed at 7.3 ppm with aromatic peaks), 8.80 ppm 1H singlet (aromatic), 9.1 ppm 1H singlet (N—H).

Preparation of 4-Nitrophenol Imprinted Polymer (IP1) via Bulk Polymerization

For the preparation of imprinted polymer (IP1), which is the noncovalent approach based on both hydrogen bonding and hydrophobic interaction, the template 4-nitrophenol (2.0 mmol) was dissolved in 22 mL of acetonitrile in a flask. The functional monomer MAAP (12 mmol), the cross-linking EGDMA (57 mmol), and the initiator AIBN (1.6 mmol) were then added to the flask. After degassing and nitrogen purging, the flask was sealed and allowed to polymerize at room temperature for 24 h under UV irradiation.

The obtained IP1 hard polymers were crushed, ground, and wet-sieved using acetone to obtain regularly sized particles between 25 and 44 μm. The polymer particles were suspended and refluxed with NaOH in methanol to remove 4-nitrophenol template molecules. The particles were then extensively washed with water and methanol until no more 4-nitrophenol was released.

Nonimprinted blank polymer in the absence of 4-nitrophenol was prepared and treated with the same method.

Preparation of 4-Nitrophenol Imprinted Polymeric Microbeads (IP2) via Suspension Polymerization

The IP2 beads were prepared by modified suspension polymerization technique. A typical suspension copolymerization procedure of IP2 beads was given as follows: The dispersion medium was prepared by dissolving 0.2 g polyvinylalcohol within 60 mL of distilled water. MAAP/4-nitrophenol (2 mmol/2 mmol) preorganized mixture and 1.05 g methylmethacrylate (MMA) were mixed into 8.0 mL EGDMA/12.0 mL toluene, and 0.100 g of 2,2′-azobisisobutyronitrile (AIBN) was dissolved within the monomer mixture. This solution was then transferred into the dispersion medium and magnetically stirred (at a constant stirring rate of 600 rpm) in a glass polymerization reactor (100 mL), which was in a thermostatic water bath. The reactor was flushed by bubbling nitrogen and then was sealed. The reactor temperature was kept at 80°C for 7 h. Then the polymerization was completed at 90°C in 3 h. After polymerization, the IP2 beads were separated from the polymerization medium. The residuals (e.g., unconverted monomer, initiator) were removed by a cleaning procedure and dried in a vacuum oven at 70°C for 48 h.

The polymer microbeads were suspended and refluxed with NaOH in methanol to remove the 4-nitrophenol template molecule. The particles were then extensively washed with water and methanol until no more 4-nitrophenol was released.

Nonimprinted blank polymer microbeads in the absence of 4-nitrophenol were prepared and treated with the same method.

IP2 microbeads were spherical in shape with a size range of 5–120 μm in diameter. The specific surface area of IP2 microbeads was found as 144.6 m^2/g. The equilibrium swelling ratio of the IP2 microbeads was determined in water at 25°C and found to be 20.5%.

Adsorption of Phenolic Compounds

Adsorption of phenolic compounds from aqueous solutions was investigated in batch experiments. Effects of the initial phenolic compounds concentration, pH of the medium on the adsorption rate, and adsorption capacity were studied. The suspensions were brought to the desired pH by adding sodium hydroxide and nitric acid. The pH was maintaned in a range of ± 0.1 units until equlibrium was attained. In all experiments, polymer concentration was kept constant at 25 mg/25 mL. The concentration of the phenolic compounds in the aqueous phases after desired treatment periods was measured by using a MECC. The experiments were performed in replicates of three, and the samples were analyzed in replicates of three as well. For each set of data present, standard statistical methods were used to determine the mean values and standard deviations. Confidence intervals of 95% were calculated for each set of samples in order to determine the margin of error. Adsorption values (mg/g) were calculated as the difference in phenolic compounds concentration of the pre- and postadsorption solutions divided by the weight of IP1 particles or IP2 microbeads.

Association constant (K_{ass}) and the number of accessible sites (N) for the specific interaction between the template imprinted polymer (IP1 and IP2) and the template itself were determined by Scathard's plots using the equation $B/F = -K_{ass}B + K_{ass}PN$, where P is the concentration of MIP, B is rebinding 4-nitrophenol concentration, and F is free 4-nitrophenol concentration.[21]

The binding ability based on molecular imprinting effect was evaluated in terms of "imprinting-induced promotion of binding" (IPB). This value is defined by

$$\mathrm{IPB} = \frac{A_{imp} - A_{non-imp}}{A_{non-imp}}$$

Here, A_{imp} is the amount of the guest that was bound by imprinted polymer under the conditions just described and $A_{non\text{-}imp}$ is the corresponding value for the nonimprinted polymer.[22]

RESULTS AND DISCUSSION

Comparison of 4-Nitrophenol Adsorption

Comparison of Adsorption Time for 4-Nitrophenol

The equilibrium adsorption time of 4-nitrophenol on the IP1 and IP2 polymers was investigated by changing the adsorption time between 15 min–12 h. These batch experiments were performed by using 4-nitrophenol solutions. The initial concentrations of phenolic compounds were kept constant at 50 mg/L. As seen in Fig. 1, adsorption amounts of phenolic compounds increased with time, and saturation levels were reached within 2 h for IP2 and around 10 h for IP1. As can be seen from the figure, 4-nitrophenol was adsorbed on IP2, which has templates by surface imprinting much faster than IP1, which has mass-transfer limitations due to bulk polymerization.

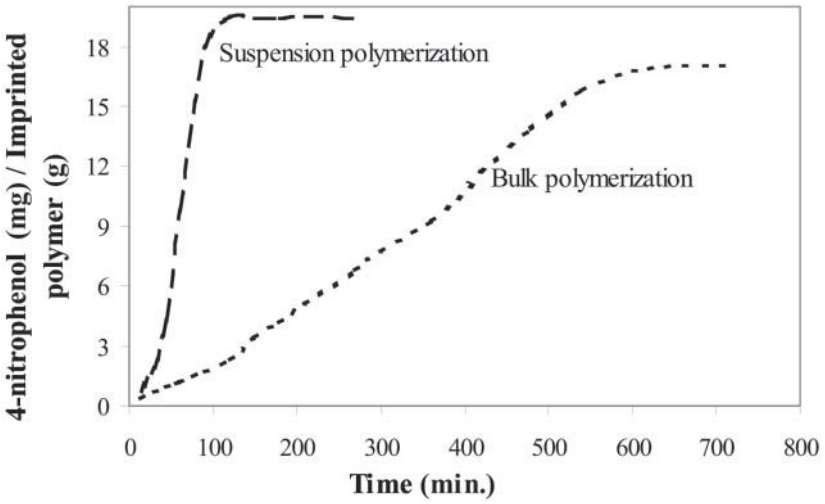

Figure 1. The adsorption rates of 4-nitrophenol on IP1 and IP2. The initial concentration of 4-nitrophenol is 50 mg/L at 25°C and pH 3.0.

The experiments related with adsorption time have been shown a wide range of adsorption rates. Ravi et al. used activated carbon for phenol and cresol adsorption[23] and Gupta et al. used ash for phenol and p-nitrophenol adsorption,[24] and they have reported 20 h and 24 h adsorption rate, respectively. The equilibrium adsorption of chlorophenol using aluminosilicate has been reported as 48 h[25] and for chloro- and nitrophenols using activated carbon has been reported as 2 weeks.[26] There are several parameters that determine the adsorption rate such as stirring rate in the aqueous phase, structural properties of sorbent-like porosity, surface area, amount of sorbent, adsorbate properties, initial concentration of phenolic species, and existence of other species. Therefore, it is too difficult to compare the adsorption rates reported. However, the adsorption rate obtained with the IP2 microbeads produced by us seem to be very satisfactory.

Comparison of Initial Concentration of 4-Nitrophenol for IP1 and IP2

Adsorption of 4-nitrophenol compounds from aqueous solutions was investigated in batch experiments. As can be seen in Fig. 2, the amount of adsorbed 4-nitrophenol per unit mass of the polymer increased with the initial concentration of the phenolic compounds. In order to reach the "saturation," the initial phenolic compounds concentrations were increased, and it was

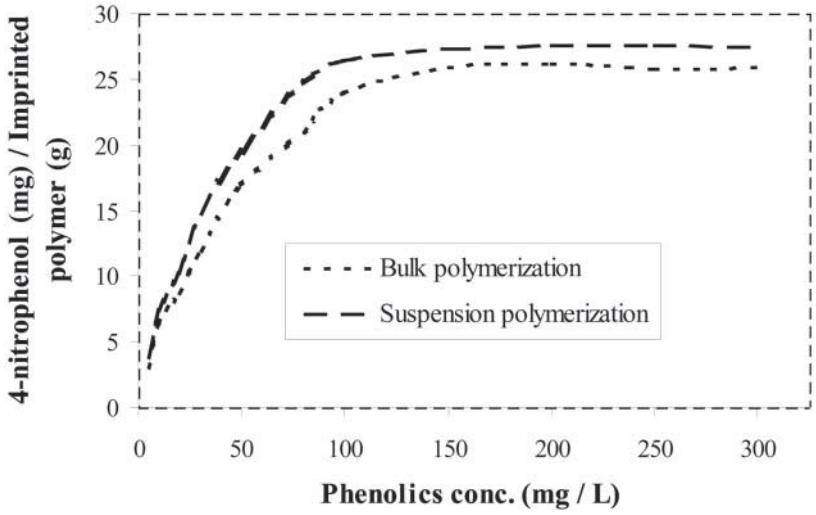

Figure 2. The 4-nitrophenol adsorption capacities of these IP1 and IP2 at 25°C and pH 3.0.

observed that the amount of adsorption was increased with the initial phenolic concentration. The maximum adsorption capacities of these IP1 and IP2 were 25.9 mg/g (187 μmol/g) and 27.6 mg/g (198.3 μmol/g) for 4-nitrophenol, respectively.

IP2-MIPs, which were prepared by suspension polymerization and based on surface imprinting, have high porosity and surface area, so there is better accessibility of the active site. Because of this, higher adsorption capacity were observed than IP1, which was prepared via bulk polymerization.

In the literature studies different adsorbents were used with a wide range of adsorption capacities for phenolic compounds. Gupta et al. showed a 60 μmol/g adsorption capacity for phenol and p-nitrophenol with a bagasse fly ash.[24] Ravi et al. reported adsorption capacities betwen 3.2 and 4.4 mmol/g with activated carbon for phenol and cresol isomers.[23] Tewari and Kamaluddin studied the removal of aminophenol and o-nitrophenol by copper, zinc, molybdenum, and chromium ferrocynanides, and they found the adsorption capacities in the range of 107–256 μmol/g for nitrophenols.[27] The adsorption capacity of nitrophenol on the poly(HEMA) (PHEMA) microbeads with Alkali Blue 6B attached was found to be 112.6 μmol/g by Denizli et al.[7]. However, note that the adsorption capacities that we achieved are comparable with the values reported in previous publications.

Effects of pH

The pH, which is the most critical parameter that effects the adsorption capacity, was determined for different pH values ranging from 2.0–9.0, using a 50.0 mg/L 4-nitrophenol. The effect of pH on adsorption of 4-nitrophenol is shown in Fig. 3. It was observed that, the phenolics binding capacity decreased with increasing pH. IP1 and IP2 exhibited a low affinity in basic conditions (pH $\geq$ 6.0). However, there is no significant decrease in the equilibrium adsorption capacity within the pH range 2.0–6.0, the highest adsorption of 4-nitrophenol occured at pH 2.0 for both IP1 and IP2.

Imprinting Efficiency to Adsorption

Binding ability to 4-nitrophenol, phenol, 2-nitrophenol, cresol, chlorophenol of IP1 and IP2 are given in Table 1. As seen from Table 1, the IPB values of imprinted-IP1 for 4-nitrophenol with respect to phenol, 2-nitrophenol, cresol, chlorophenol is higher than the IPB values of nonimprinted IP1. The same was observed for IP2, and 4-nitrophenol is adsorbed more efficiently than other phenolics. Imprinted IP2 has higher adsorption selectivity than nonimprinted

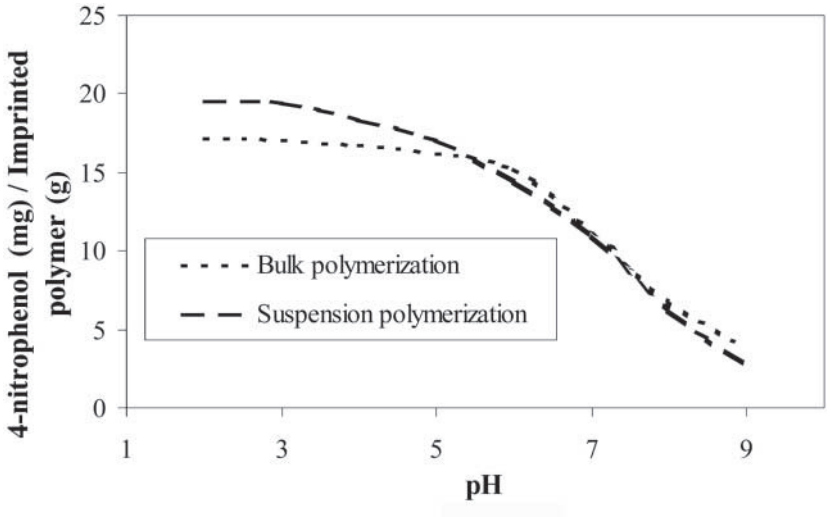

Figure 3. The effect of pH on the adsorption of 4-nitrophenol on the microbeads at 25°C and initial compounds of 50 mg/L.

IP2 for 4-nitrophenol. It can be obviously seen that imprinted IP1 and IP2 polymers are more selective than nonimprinted polymers because the imprinted polymers, are memorized in the structures of the 4-nitrophenol templates and so they have suitable size and shape of cavity for 4-nitrophenol. IP2 has higher IPB value than IP1 for 4-nitrophenol with respect to other phenolic compounds. As it was mentioned before, this may be because of surface imprinting of IP2, which has high porosity and surface area (the specific surface area of IP1 and IP2 were found to be 130.3 and 207.6 m^2/g, respectively) and better accessibility of the active site. The template can

Table 1. Binding ability of 4-nitrophenol imprinted polymers IP1 and IP2 toward phenolics.

	IP1			IP2		
Phenolics	Imp. (mg/g)	Non-Imp. (mg/g)	IPB	Imp. (mg/g)	Non-Imp. (mg/g)	IPB
4-Nitrophenol	21.2	9.1	133	24.8	10.3	141
Chlorophenol	17.3	9.4	84	13.5	10.4	30
2-Nitrophenol	15.5	8.7	78	11.7	9.1	29
Cresol	16.1	9.3	73	12.4	9.1	15
Phenol	13.2	7.4	24	9.8	8.6	14

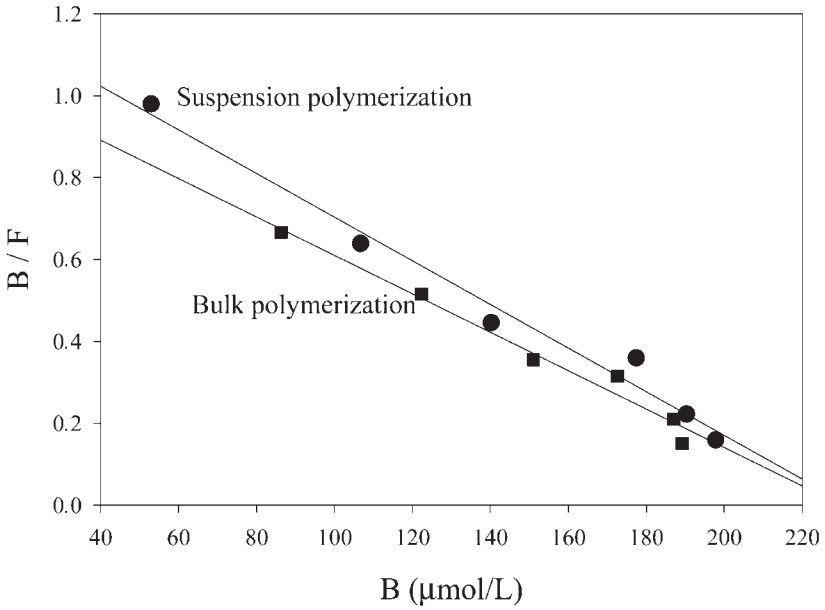

Figure 4. Scatchard's plot of 4-nitrophenol rebinding by the imprinted polymers; Concentration of polymer: 25 mg/25 mL.

easily not react with the cavity when the bulk polymerization technique was applied.

K_{ass} and the N values for the specific interaction between the template imprinted polymer and the template itself were determined by Scatchard's plots using both IP1 and IP' polymers. K_{ass} and the N values can be estimated as $4.7 \times 10^3\,mol^{-1}\,2\,L$ and $1.08\,\mu mol/g$ for IP1 and $5.3 \times 10^3\,mol^{-1}\,L$ and $1.24\,\mu mol/g$ for IP2, respectively, from the slope and the intercept in Fig. 4. Comparing IP1 with IP2, higher K_{ass} and the N values were obtained in the IP2 imprinted system. This can be explained again for the same reason, IP2 has high porosity, surface area, and the active site, and so has high-adsorption capacity.

CONCLUSION

The development of an effective technology for the removal of phenolic compounds from wastewater is important because of its carcinogenic property and pollutant effect. For this purpose, using an adsorptive resin for the removal of phenolic compounds could be a method of choice.

In this study, a new polymer with memory was prepared for the selective removal of phenolic compounds from wastewater. By considering this purpose, 4-nitrophenol imprinted polymers were synthesized using MAAP monomer, applying both bulk (IP1) and suspension (IP2) polymerization techniques. The effects of these polymers and polymerization techniques on 4-nitrophenol and other phenolics adsorption were investigated. IP2-MIPs, which were prepared by suspension polymerization and based on surface imprinting, have high porosity and surface area, and so have better accessibility of the active site. Because of this, higher adsorption capacity was observed than IP1, which was prepared via bulk polymerization. The maximum adsorption capacities of these IP1 and IP2 were 25.9 and 27.6 mg/g for 4-nitrophenol, respectively. IPB values of IP1 and IP2 for phenol, 2-nitrophenol, cresol, chlorophenol showed that both IP1 and IP2 have significant selectivity to 4-nitrophenol, and it was observed that IP2 has the higher binding capacity compared to IP1. The same results were also obtained using Scatchard's plot.

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